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The objective of the research project is to explore the unimolecular and collisional excitation and decay mechanisms, reactivity and detectivity of molecules in metastable triplet states. The two primary research accomplishments are: (1) formulation and testing of a new and rigorous deconvolution procedure to completely characterize the mechanism of doorway mediated inter-system crossing and (2) observation of Franck-Condon and energy resonance controlled electronic excitation transfer between Xe 3P2 metastable atoms and N2 molecules.

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Page One

1. **Principal InvestigatorName:**

   Robert W. Field

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6. **Program Manager:**

   Michael R. Berman

7. **Annual Accomplishments (200 words maximum):**

   The objective of the research project is to explore the unimolecular and collisional excitation and decay mechanisms, reactivity, and detectivity of molecules in metastable triplet states. The two primary research accomplishments are: (1) formulation and testing of a new and rigorous deconvolution procedure to completely characterize the mechanism of "doorway mediated inter-system crossing;" and (2)observation of Franck-Condon and energy-resonance controlled electronic excitation transfer between Xe 3P2 metastable atoms and N2 molecules.

8. **Archival Publications (published) during reporting period:**

   R. W. Field, O. Pirali, and D. W. Tokaryk, J. Chem. Phys. 124, 081103 (2006)
   B. M. Wong, R. L. Thom, and R. W. Field, J. Phys. Chem A 110, 7406 (2006)
   R. L. Thom, B. M. Wong, R. W. Field, and J. L. Stanton, J. Chem. Phys. 126, 184307 (2007)
   W. L. Virgo, K. L. Bittinger, A. H. Steeves, and R. W. Field, J. Phys. Chem. A 111, 12534 (2007)

9. **Changes in research objectives (if any):**

   None.

10. **Change in AFOSR program manager, if any:**

    None.

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11. Extensions granted or milestones slipped, if any:

No cost extension from 12/31/2007 to 06/30/2008.

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I. STAFF SUPPORTED BY AFOSR GRANT

A. Postdocts

1. Wilton Virgo currently Assistant Professor, Wellesley College
2. Hans Bechtel, currently Scientist, Lawrence Berkeley National Lab
3. Kirill Kuyanov, MIT
4. Jonathan Smith, Professor, Gustavus Adolphus College

B. Graduate Students

1. Ryan Thom, January,2005 - March, 2006 currently S.A.C. Capital Advisors
2. Kyle Bittinger, MIT January, 2005 - June, 2008
3. Samuel Lipoff, MIT (DHS and NSF Graduate Fellow) September-November, 2006
4. Erika Robertson, MIT January-March, 2008
5. Bryan Wong, June, 2006 - March, 2007 currently at Sandia National Laboratories

C. Undergraduate Students

1. Jessica Lam, July-September, 2006
2. Yuki Jung
3. Katie Silberstein
4. Lauren Hakes
5. Edwin Guerrero
6. Meghan Reedy
7. Phillip Lichtor
8. Sylvia Robles
9. Annelise Beck

II. Research Accomplishments (1 January 2005 - 30 June 2008)

The following is a slightly edited version of the "Accomplishments" section of the pending three-year Renewal Proposal submitted February, 2008.

The experimental results that most conclusively demonstrate the feasibility and dynamical richness of the proposed ion-imaging experiments are the observation, in SEELEM-TOF spectra, of temporally resolved features associated with product states distinguished by their expected momentum kick (see Figures 2 and 6). In the $Xe^{\star}$+N_2 $\rightarrow$Xe + $N_2(B^3\Pi_g v')$ excitation transfer reaction, peaks in Figure 2 (trace of Xe in N_2, $Xe^{\star}$ excited in the high pressure region just in front of the nozzle) at 610, 390, and 210 μs are associated with $Xe^{\star}$, $N_2(v'=5)$, and $N_2(v'=4)$. The $N_2^{\star}$ formed by excitation transfer from $Xe^{\star}$ is isotropically distributed in the center-of-mass coordinate system. As a result, the actual $N_2^{\star}$:Xe and $N_2^{\star}(v=4)$:$N_2^{\star}(v=5)$ population ratios are larger by factors of 10^3 and 3.5, respectively, than the ratios of peak areas in the TOF spectrum. A jet of Xe excited to $Xe^{\star}(^3P_2)$ just in front of the nozzle, yields assignable features in the SEELEM-TOF spectrum that are due to $Xe^{\star}$(844μs), $Xe^+(^2P_{3/2})$ (361μs), and $Xe^+(^2P_{1/2})$ (472μs) where the Xe^+ is produced by the Penning ionization reaction $Xe^{\star}$+ $Xe^{\star}$ $\rightarrow$Xe + $Xe^+(^2P_J)$ (see Figure 6). Xe^+, formed by multiphoton ionization of Xe, and Xe_2^+, formed by $Xe^\star$+$Xe^\star$ →Xe_2^+ associative ionization, receive no momentum kick and arrive in coincidence with $Xe^\star$. Neutral metastables are distinguished from ions when a deflection field sweeps the ions off of the SEELEM detector.

The experimental component of greatest importance for the proposed $Hg^\star$ electronic excitation transfer experiments is the heated (T < 600 K) pulsed valve, constructed for us by the University of Bern machine shop, following the design of Professor Samuel Leutwyler.

The mechanism of the doorway-mediated intersystem crossing in HCCH was subjected to systematic analysis. Highly excited "dark" vibrational levels of the $T_{1,2}$ states are indirectly illuminated by an S_1 "bright" state via one or two T_3 "doorway" states. The existence of this doorway mechanism has been the subject of several experimental and theoretical studies.We have uncovered several crucial features of this doorway mechanism.

- The topography of the T_3 adiabatic potential surface is exceptionally complicated near its minimum, owing to two seams of conical intersection with the T_2 surface. The $T_3 \sim T_2$ interacting potential surfaces are transformed to a diabatic representation. The diabatic T_3 potential exhibits a regular, albeit nonplanar equilibrium structure. The vibrational normal modes for the diabatic T_3 potential are derived and used to compute vibrational overlap integrals with nearby S_1 vibrational levels. The vibrational overlap integrals, in combination with the calculated $S_1 \sim T_3$ electronic spin-orbit matrix element and the vibronic spin-orbit interaction matrix elements measured at two perturbations of the S_1 $3\nu_3$ vibrational level, result in two vibrational assignment possibilities for the T_3 perturbing level.
- Previous studies of $S_1 \sim T_{1,2}$ spin-orbit perturbations (Zeeman Anti-Crossings and Quantum Beats) have suggested that, despite the nonplanar near-trans equilibrium geometry of the T_3 state, that the S_1 torsion (ν_4) and "*cis*-bending" (ν_6) vibrations respectively suppress and enhance $S_1 \sim T_3 \sim T_{1,2}$ doorway-mediated interactions. However, systematic studies of the anharmonic and Coriolis interactions in the S_1 state reveal profound $\nu_4 \sim \nu_6$ mixing. One example is the 50 : 50 mixed $2^1 3^1 4^2 \sim 2^1 3^1 6^2$ $K_a = 1$ pair of interacting states. Despite the 50 : 50 mixing, the SEELEM spectra recorded near each of these two 50 : 50 mixed states exhibits profoundly different level patterns and total intensities. The paradox is resolved by an interference effect. One member of the 50 : 50 mixed pair of levels mixes (a–type Coriolis) with the $2^1 3^1 4^1 6^1$ $K_a = 1$ level, but this Coriolis interaction is suppressed by destructive interference for the other mixed level. The strong SEELEM spectrum is observed near the mixed S_1 state that has significant admixed $2^1 3^1 4^1 6^1$ character.
- The previous null conclusion about whether ν_4 or ν_6 promotes coupling to T_3 led us to design an experiment involving S_1 vibrational levels where both anharmonic and Coriolis interactions between modes ν_4 and ν_6 are turned off. These are the rigorously non-interacting $3^3 4^1$ and $3^3 6^1$ $K_a = 0$ levels, accessed via IR-UV double resonance. Our SEELEM spectra via this double resonance excitation path were the most intense and highest quality SEELEM spectra we have ever recorded (see Figure 7). They are being subjected to a variety of statistical and effective Hamiltonian pattern extraction schemes, one of which is described below. But the key result is that, as expected based on the non-planar geometry of the diabatic T_3 state, the S_1 torsional mode promotes coupling with $T_{1,2}$ via the T_3 doorway.

- We have discovered a rigorous extension of the "Lawrance-Knight (LK)" deconvolution procedure to extract, from an LIF spectrum, the deperturbed energies of the "bright", "doorway", and dark states and the doorway$\sim$bright coupling matrix element. The LK procedure was devised to deal with a direct bright$\sim$dark coupling situation. Our extended LK procedure has been applied to the exceptionally high quality Drabbels LIF data for the HCCH $3\nu_3$ level. The derived energies and coupling matrix elements agree with results obtained via conventional effective Hamiltonian fits. However, most significantly, the extended LK procedure uncovers a pattern of derived J–dependent coupling matrix elements that suggests the occurrence of a "double-doorway" interference situation. Interference in the coupling between S_1 and $T_{1,2}$ occurs in both doorway paths, one via an energetically remote strong $S_1 \sim T_3$ perturber and the other via a weak local $S_1 \sim T_3$ perturber.

- This double-doorway situation was initially uncovered in collaboration with Professor Wybren Jan Buma and Dr. Mattijs De Groot at the University of Amsterdam. Owing to the different patterns of Franck-Condon factors for transitions to the $HCCH^+$ molecular-ion state from S_1 $3\nu_3$, T_3, and $T_{1,2}$ the Photo-Electron Spectrum (PES) displays a dip in the intensity of features associated with $T_{1,2}$ eigenstate character precisely in the region of the S_1 $3\nu_3 \sim T_3$ local doorway level crossing. A dip rather than a maximum implies destructive interference between local-doorway and remote-doorway Inter-System Crossing (ISC) pathways. This demonstration of interference between two ISC pathways invites novel schemes for external control over ISC.

- In collaboration with Trevor Sears (Brookhaven) we recorded SEELEM spectra of phenyl-acetylene (PA), with detection of T_1 PA on Yttrium. The SEELEM/LIF intensity ratio varied from one band to another, suggesting that the $S_1 \sim T_1$ coupling strength depends on the S_1 vibrational level in a way that is different from the Franck-Condon factors for $S_1 \leftarrow S_0$ excitation.

Several papers, based on chapters in Kyle Bittinger's Ph.D. Thesis, are in final preparation for publication.

1. Deconvolution of spectral data to extract the parameters that define a doorway-coupling model Hamiltonian. (Bittinger Thesis: Chapter 3.)
2. Communication: Signatures of doorway-mediated intersystem crossing in delayed, incoherent fluorescence measurements. This paper demonstrates the experimental technique of time-gated LIF and the deconvolution software that determines the energy, spin-rovibronic assignment, and coupling matrix elements of the doorway state. (Bittinger Thesis: Chapter 4, section 2.)
3. Invited feature article in *J. Chem. Phys.* "SEELEM/LIF Spectroscopy of Acetylene: Spectral Signatures of Energetically Distant Doorway States". (Bittinger Thesis: Chapter 4.)

   Our highest quality spectra, of the acetylene $\tilde{A}$–state $2^1 3^2$, $2^2 3^1$, $3^2 4^2$, $3^2 6^2$, and 3^3 vibrational levels, are used to sample many doorway states and to generalize on the Franck-Condon patterns in $S_1 \sim T_3$ (doorway) interactions.
4. IR-UV double resonance SEELEM spectroscopy of the $3^3 B^1$ ungerade bending polyad of S_1 acetylene. By looking at iso-energetic S_1 $3^3 4^1$ and $3^3 6^1$ $K = 0$ vibrational levels that cannot interact either by Coriolis ($K = 0$) or anharmonic mechanisms, the Franck-Condon propensity rules for $S_1 \sim T_3$ (doorway) interactions are revealed. [Bittinger Thesis, Chapter 6.]

5. Communication. Direct Observation of acetylene $T_{1,2}$ state density in the SEELEM spectrum of the S_1 $3^3 6^1 J = K = 0$ level.

6. Evidence for a singlet∼triplet dynamical double doorway in the acetylene $\widetilde{A}^1A_u - X^1\Sigma_g^+$ $V_0^3 K_0^1$ band.

III. AFOSR Supported Publications (since 2000)

265. M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, and P.S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments", *J. Phys. Chem.* **104**, 249–257 (2000).

269. M. Joyeux, D. Sugny, V. Tyng, M.E. Kellman, H. Ishikawa, R.W. Field, C. Beck, and R. Schinke, "Semiclassical Study of the Isomerization States of HCP", *J. Chem. Phys.* **112**, 4162–4172 (2000).

273. A.F. Ruckstuhl, M.P. Jacobson, R.W. Field, and J.A. Dodd, "Baseline Subtraction Using Robust Local Regression Estimation", *J. Quant. Spectr. Radiat. Transf.* **68**, 179–193 (2001).

278. S. Altunata and R. W. Field, "A Statistical Approach for the Study of the Singlet–Triplet Interactions in Small Polyatomic Molecules", *J. Chem. Phys.* **113**, 6640–6651 (2000).

282. E. S. Hwang, J. B. Lipson, R.W. Field, and J. A. Dodd, "Detection of OH(X, v'', J'') via the $B\ ^2\Sigma^+ - X\ ^2\Pi$ Transition and Properties of the $B\ ^2\Sigma^+$ State", *J. Phys. Chem.* **105**, 6030 – 6037 (2001).

283. M. Silva, R. Jongma, R.W. Field, and A.M. Wodtke, "The Dynamics of 'Stretched Molecules': Experimental Studies of Highly Vibrationally Excited Molecules with Stimulated Emission Pumping", *Ann. Rev. Phys. Chem.* **52**, 811–852 (2001).

284. S. Altunata and R. W. Field, "An Assumption–Violating Application of the Lawrance–Knight Deconvolution Procedure: A Retrieval of Electronic Coupling Mechanisms Underlying Complex Spectra", *J. Chem. Phys.* **114**, 6557–6561 (2001).

287. S. Altunata, K. L. Cunningham, M. Canagaratna, R. Thom and R. W. Field, "The Mechanism of Surface Electron Ejection by Laser Excited Metastable Molecules", *J. Phys. Chem.* **106**, 1122-1130 (2002).

293. A. P. Mishra, R. L. Thom, S. Altunata, and R. W. Field, "Study of Intramolecular Dynamics of Highly Energized Small Molecules Using Laser Spectroscopic Techniques", in *Current Developments in Atomic, Molecular, and Chemical Physics with Applications* (ed. Man Mohan), 2003, Kluwer, New York.

301. A. P. Mishra, R. L. Thom, and R. W. Field, "New S_1 State Vibrational and $T_{3,\ 2,\ 1}$ Spin-Rotational Assignments in the Vicinity of the Acetylene $\widetilde{A}^1A_u - \widetilde{X}^1\Sigma_g^+$ $V_0^3 K_0^1$ Band," *J. Mol. Spectrosc.* **228**, 565-579 (2004).

314. R. W. Field, O. Pirali, and D. W. Tokaryk, "The Spin-Orbit and Rotational Constants for the N_2 $C''\ ^5\Pi_{ui}$ ($v = 3$) State," *J. Chem. Phys.* **124**, 081103-1 - 081103-3 (2006).

317. B. M. Wong, R. L. Thom, and R. W. Field, "Accurate Inertias for Large-Amplitude Motions: Improvements on Prevailing Approximations," *J. Phys. Chem. A* **110(23)**, 7406-7413 (2006).

319. R. L. Thom, B. M. Wong, R. W. Field, and J. F. Stanton, "Studies of Intersystem Crossing Dynamics in Acetylene," *J. Chem. Phys.* **126**, 184307/1-7 (2007).

324. W. L. Virgo, K. L. Bittinger, A. H. Steeves, and R. W. Field, "Contrasting Singlet-Triplet Dynamical Behavior of Two Vibrational levels of the Acetylene S_1 $2^1 3^1 B^2$ Polyad, *J. Phys. Chem.* **111**, 12534-12537 (2007).

327. M. de Groot, R. W. Field, and W. J. Buma, "Interference in Intersystem Crossing in Acetylene," *Phys. Rev. Lett.* (submitted).

IV. New Discoveries, Inventions, and Patents

None.

V. Honors

Robert Field:	Bomem-Michelson Award, Coblentz Society (2006)
Robert Field:	Elected to Fellowship in the American Association for the Advancement of Science (2002)
Wilton Virgo:	MIT's Martin Luther King Postdoctoral Fellow (2006-2008)
Adam Steeves:	Coblentz Society Student Award (2007)
Annelise Beck:	Goldwater Scholarship (2008)